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Interlaboratory Study 2002-2

N-Nitrosodimethylamine In Drinking Water

March 2003



Ministry of the
Environment

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Interlaboratory Study 2002-2 N-Nitrosodimethylamine In Drinking Water

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Laboratory Services Branch
Ontario Ministry of the Environment

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Harold Hodgson, Area Manager of Water
Niagara Falls Water Treatment Plant

Steve Green, Provincial Officer
Niagara District - Ministry of the Environment

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1. INTRODUCTION

The Laboratory Services Branch (LSB) of the Ontario Ministry of the Environment (MOE), initiated Interlaboratory Study 02-2, N-Nitrosodimethylamine (NDMA) in Drinking Water, to evaluate interlaboratory performance and investigate possible method biases. The reason for this interlaboratory study (ILS) was based on the MOE receiving reports of NDMA exceedances in drinking water over the 6 month period prior to the study date (late 2001 through early 2002). Drinking water exceedances are based on the Ontario Drinking Water Standards¹ and Ontario Regulations 459/00² and 505/01³. Findings from the preliminary investigation by the MOE suggested that the problem may be an analytical method bias due to unknown matrix effects, rather than a problem with the water treatment process.

Environmental analytical laboratories that were accredited by the Standards Council of Canada (SCC) for the analysis of NDMA in drinking water were invited to participate in this study.

2. STUDY DESIGN

2.1 Source of Materials

The study design consisted of spiking reagent water (LSB Pure Water - laboratory reverse-osmosis water that had been further treated with an organic removal cartridge and two deionizer cartridges) and a bulk drinking water sample with the LSB Quality Management (QM) Unit's NDMA spiking standard routinely used for the internal Performance Evaluation Program (PEP).

The bulk drinking water sample was collected from the Niagara Falls Water Treatment Plant on June 24, 2002. It was collected from a continuously flowing tap in the plant's on-site laboratory, into stainless steel tanks and brought back to LSB for homogenizing. It was kept refrigerated (<10°C) until ready for use.

The reagent water was collected into a large container on the day that the ILS samples were prepared, July 2, 2002.

The spiking standard was purchased from Supelco, Lot # LA21457. The spiking solution was prepared in HPLC grade methanol and sealed into 2 mL amber ampoules.

2.2 Sample Preparation

For each spiked sample (reagent water or Niagara water), a bulk sample was prepared by transferring five, 2000 mL aliquots of the matrix from the bulk container into a separate stainless container, using a Class A volumetric flask. Prior to filling the flask to the mark for the first aliquot of matrix, the required amount of NDMA spiking solution was added to the flask. For each 2000 mL aliquot of matrix, the flask was weighed before filling, and after transferring the

matrix to the stainless steel container. After all five aliquots were added to the stainless steel container, the bulk, spiked sample was stirred. The bulk sample, with constant stirring, was then dispensed into 1 litre, amber glass bottles and labeled as listed in Table 1.

For the unspiked reagent water and unspiked Niagara water samples, the individual 1 litre amber bottles were filled directly from the original, bulk matrix containers (see 2.1). The bottles were labeled as listed in Table 1.

TABLE 1 - SAMPLE PREPARATION		
SAMPLE ID	MATRIX	NDMA DESIGN CONC. (ng/L)
1	Niagara water	0
2	Reagent water	12.21
3	Reagent water	0
4	Niagara water	16.28
5	Niagara water	8.14
6	Niagara water	24.42

2.3 Sample Distribution

Six Canadian environmental laboratories agreed to participate in this study. All participants were assigned an identification code.

Sample sets, consisting of the six one litre amber bottles, were sent by courier to the participants on July 3, 2002. An instruction sheet and report form was included with the samples, as well as a methodology questionnaire. Examples are included in Appendix 5. Electronic versions of the report form and methodology questionnaire were provided by e-mail to all of the participants.

3. STUDY RESULTS

Results were reported electronically by all six participants.

A preliminary table of results was distributed to the participants on November 24, 2000. Two participants reviewed their work and provided revised data. The final data set is provided in Appendix 1, Table 2.

The percent recovery of the design value was calculated for the data set and is included in Appendix 1, Table 2. As the data set is small (<10 data points) and not normally distributed, no statistical calculations were done.

To aid in the interpretation of the results, a graphical presentation of the data as percent recovery of the design values, in a bar chart format, is provided in Appendix 2. The instrumentation used by each participant is also indicated on the graph.

A summary of the methodology questionnaire is provided in Appendix 3.

4. DISCUSSION

The results from the six participants show three groups of data: laboratories 2201, 2203 and 2205, laboratories 2204 and 2206, and laboratory 2202 separate from the others (Appendix 1, Table 2). This is also clearly seen in the graphical presentation in Appendix 2.

The grouping of the participants' results appear to be related to the methodology used for the analysis, as identified in Appendix 2. Sample preparation does not appear to be a factor, as all six laboratories used similar extraction techniques, all with the same solvent. (Appendix 3, Table 3). None of the participants used a clean-up procedure for these samples (Appendix 3, Table 3).

Laboratory 2202 was the only participant to use HPLC-DAD to analyze these samples. Their results are very different from the others. Only a limited amount of information on their methodology was provided. Possible sources for the high bias in their results include insufficient resolution in their chromatography, or interferences from other compounds with a Nitrogen-Oxygen bond absorbing at the same wavelength. This method does not appear to be appropriate for the analysis of NDMA at low concentration levels in drinking water matrices.

Laboratory 2206 indicated that they had participated in this study as a method development exercise (see Additional Comments at the end of Methodology Summary, Appendix 3). All of their data was reported with a "<" qualifier (Table 2). They achieved good recovery relative to the design value for Sample 6, the highest concentration sample in the study, but were biased high for the other three spiked samples. This suggests that their GC/LRMS method may be sufficiently sensitive to approximately 25 ng/L, but is not suitable for NDMA samples at lower concentrations. The comment provided by this laboratory indicates that they recognize the limitations of their methodology.

Laboratory 2204 had good recovery relative to the design value, for the spiked reagent water sample (Sample 2), but were biased high for the spiked Niagara water samples (Samples 4, 5 and 6). At low levels, a deviation of approximately $\pm 30\%$ may be expected. Laboratory 2204's results for Samples 4, 5 and 6 differed from the design values by $>100\%$ (Table 2, Appendix 1). They also reported a positive value for the unspiked Niagara water sample (Sample 1) that was well above the detection limit. These results suggest that this laboratory's method has an artifact problem with the treated drinking water matrix used in this study.

The three laboratories using GC/HRMS (2201, 2203 and 2205) reported similar results for all six samples. All three laboratories have instruments from different manufacturers, but they all used the same chromatographic column. Laboratories 2203 and 2205 may have a slight artifact effect at very low levels, as they were slightly high for Sample 5, the sample spiked with the smallest concentration of NDMA.

5. CONCLUSION

The distribution of the results from this study demonstrates good agreement with the design values, for laboratories using GC/HRMS to analyze drinking water matrix samples. Laboratories using other instrumental techniques (GC/MS/MS, GC/LRMS, or HPLC-DAD) were not able to achieve the low-level target values in the drinking water matrix. Based on this limited data set, it appears that GC/HRMS is the only instrumental technique suitable at the present time to analyze low-level NDMA in drinking water matrix samples.

6. BIBLIOGRAPHY

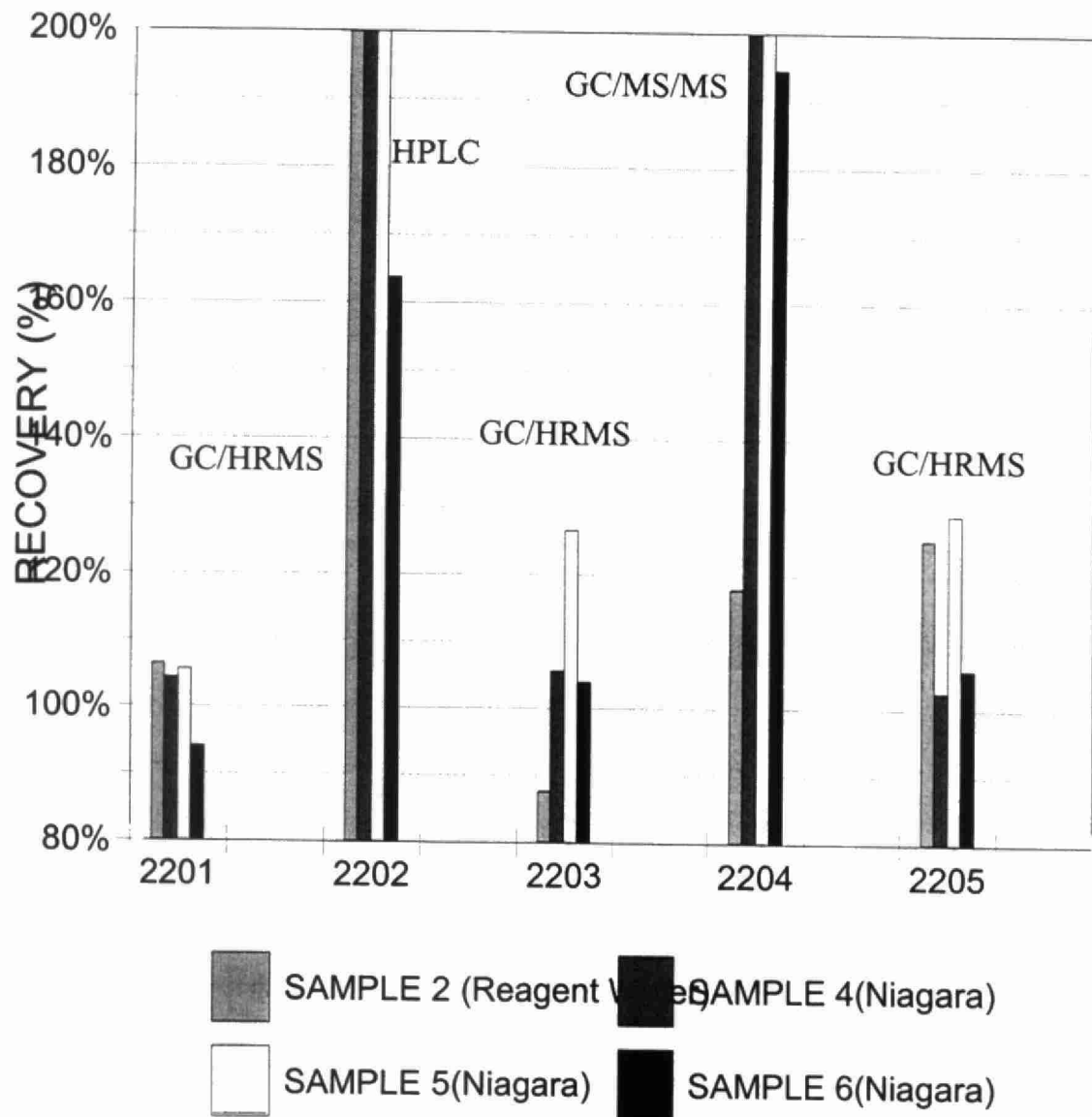
1. MOE Ontario Drinking Water Standards; January 2001
2. Drinking Water Protection - Larger Water Works, O. Reg. 459/00, Amended to O. Reg. 213/02
3. Drinking Water Protection - Smaller Water Works Serving Designated Facilities, O. Reg. 505/01

TABLE 2 - PARTICIPANTS' RESULTS

	Matrix*	Design ng/L	2201		2202		2203		2204		2205		2206	
			RESULT ng/L	RECOVERY %	RESULT ng/L	RECOVERY %	RESULT ng/L	RECOVERY %	RESULT ng/L	RECOVERY %	RESULT ng/L	RECOVERY %	RESULT ng/L	RECOVERY %
SAMPLE 1	Niagara	0	1<MDL		39		2.7		15.4		1.83		<7	
SAMPLE 2	Reagent Water	12.21	13	106.5%	108	884.5%	10.7	87.6%	14.4	117.9%	15.3	125.3%	<19	155.6%
SAMPLE 3	Reagent Water	0	1<MDL		112		1.3		1		1.5		<15	
SAMPLE 4	Niagara	16.28	17	104.4%	133	817.0%	17.2	105.7%	34.5	211.9%	16.7	102.6%	<26	159.7%
SAMPLE 5	Niagara	8.14	8.6	105.7%	170	2088.5%	10.3	126.5%	28.5	350.1%	10.5	129.0%	<17	208.8%
SAMPLE 6	Niagara	24.42	23	94.2%	40	163.8%	25.4	104.0%	47.5	194.5%	25.9	106.1%	<27	110.6%

* **Reagent Water** LSB Pure Water that has been further treated
Niagara Treated water from Niagara Water Treatment Plant

APPENDIX 2 - GRAPH



APPENDIX 3 - METHODOLOGY SUMMARY

TABLE 3 - Methodology Summary														
Sample Storage	Refrigerated, in dark	6 labs												
Sample Extraction Volume	500 mL 1000 mL 1600-1650 mL	2 labs 3 labs 1 lab												
Extraction Technique	Ambersorb 572 beads Liquid-Liquid extraction Serial solvent partition	1 lab 4 labs 1 lab												
Extraction solvent	Dichloromethane	6 labs												
Source of labeled standard	MSD Isotopes CDN Cambridge Isotopes Laboratories None	2 labs 3 labs 1 lab												
Final sample volume	100 µL 400 µL 500 µL 1.0 mL	2 labs 1 lab 2 labs 1 lab												
Clean-up	None performed													
GC Column	DB 1701, 30 m x 0.25 mm x 0.25 µm OV-5 Amine, 30 m x 0.25 mm x 0.25 µm Restek Stabilwax, 30 m x 0.25 mm x 0.25 µm No information provided on HPLC column	3 labs 1 lab 1 lab 1 lab												
Injector	Splitless No information provided	5 labs 1 lab												
GC Temperature Program	<table><tr><td><u>Start</u></td><td><u>End</u></td></tr><tr><td>38°C</td><td>250°C</td></tr><tr><td>30°C</td><td>200°C</td></tr><tr><td>n/a</td><td>180°C</td></tr><tr><td>60°C</td><td>220°C</td></tr><tr><td colspan="2">Not applicable</td></tr></table>	<u>Start</u>	<u>End</u>	38°C	250°C	30°C	200°C	n/a	180°C	60°C	220°C	Not applicable		2 labs 1 lab 1 lab 1 lab 1 lab
<u>Start</u>	<u>End</u>													
38°C	250°C													
30°C	200°C													
n/a	180°C													
60°C	220°C													
Not applicable														
Carrier Gas	Helium	5 labs												
Mode	Constant Pressure Constant Flow	1 lab 4 labs												
Instrumentation	GC/HRMS GC/MS/MS GC/LRMS HPLC-DAD	3 labs 1 lab 1 lab 1 lab												
Resolution of HRMS	7000 7500	2 labs 1 lab												

TABLE 3 - Methodology Summary		
Source of Calibration Standard	Supelco Ultra Scientific Accustandard No information provided	3 labs 1 lab 1 lab 1 lab
Type of Calibration	Multi-point Multi-point with continuing calibration No information provided	2 labs 3 labs 1 lab
Injection Volume	2 μ L 3 μ L No information provided	4 labs 1 lab 1 lab
Correct for Recovery	Yes	6 labs
Quantitation Procedure	Isotope Dilution Internal Standard No information provided	4 labs 1 lab 1 lab
Laboratory Accredited	Yes No	5 labs 1 lab
PE Program Participation	Yes (California DHS NDMA PE Study) No	2 labs 4 labs
Years Experience Analyzing NDMA	<5 5 - 10 >10	2 labs 2 labs 2 labs
Annual NDMA Workload	< 200 samples 200 - 500 samples 500 - 1000 samples > 1000 samples Variable	1 lab 2 labs 1 lab 1 lab 1 lab

Additional Comments

Laboratory 2206 is not accredited for analyzing NDMA in drinking water, and participated in this study to help establish lower MDL's for their clients. They noted that they would not use their GC/LRMS method for Ontario drinking water samples, as they feel that GC/HRMS is necessary.

APPENDIX 4 - LIST OF PARTICIPANTS

Maxxam Analytics Inc., Waterloo, Ontario

Ontario Ministry of the Environment, Laboratory Services Branch, Etobicoke, Ontario

Philip Analytical Services, Burlington Laboratory, Burlington, Ontario

Research Productivity Council (RPC), Fredericton, New Brunswick

SAIC Laboratory, Gloucester, Ontario

SGS Lakefield Research Limited, Lakefield, Ontario

APPENDIX 5 - CORRESPONDENCE

INVITATION FOR PARTICIPATION IN MOE INTERLABORATORY STUDY 02-2

The Ontario Ministry of the Environment (MOE) has received reports of N-Nitrosodimethylamine (NDMA) exceedances in drinking water over the past 6 months. Findings from the preliminary investigation by the MOE suggest that the problem may be an analytical method bias due to unknown matrix effects, rather than a problem with the water treatment process.

The Laboratory Services Branch (LSB) of the MOE, is conducting an interlaboratory study (ILS) of NDMA in drinking water, to evaluate interlaboratory performance and investigate possible method biases. As an SCC-accredited laboratory for NDMA analysis in drinking water, we would appreciate your assistance in assessing the situation by participating in this ILS.

The anticipated date for sample distribution is the week of March 11, 2002 and the results are expected to be reported by April 26, 2002. The study is expected to consist of six (6) samples. There is no fee for participation in this study.

If you are interested in participating, please complete the response form (enclosed) and return by February 15, 2002. If there are any questions you would like to ask before accepting, please do not hesitate to contact either Sylvia Cussion or Sathi Selliah.

Sylvia Cussion
phone: 416-235-6348
Fax: 416-235-6312
email: cussionsy@ene.gov.on.ca

Sathi Selliah
Phone: 416-235-5700
Fax: 416-235-6312
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Mailing Address:

Ontario Ministry of the Environment
Laboratory Services Branch
125 Resources Road
Etobicoke ON, M9P 3V6 Canada

INTERLABORATORY STUDY 02-2
N-NITROSODIMETHYLAMINE IN DRINKING WATER

NAME: _____ <div style="text-align: right; font-size: small;">(Please Print)</div>		
INSTITUTE/COMPANY: _____ <div style="text-align: right; font-size: small;">(Please Print)</div>		
SHIPPING ADDRESS: _____ <div style="text-align: right; font-size: small;">(Please Print)</div> _____ _____		
Tel: _____		
FAX: _____		
E-mail: _____		
Will participate in MOE ILS 02-2	YES	NO
Minimum sample volume required: _____		
Solvent required for instrument-ready injection: _____		

SIGNATURE: _____ **DATE:** _____

Please return this sheet to:

Sylvia Cussion, ILS Coordinator
Ministry of the Environment,
Laboratory Services Branch
125 Resources Road
Etobicoke, ON M9P 3V6
Fax: (416) 235-6312
Quality Management Unit

July 3, 2002

Name
Organization
Address

RE: MOEE Interlaboratory Study 02-2

Please find enclosed the samples and supporting materials for MOEE Interlaboratory Study 02-2, N-Nitrosodimethylamine in Drinking Water. Please contact either of us immediately if any of the sample containers have been broken during shipping, and we will provide replacements.

The following has been provided to each participant:

6 Samples (1 litre each)

Electronic report forms on 3.5" diskette: Data.xls and Questionnaire.wpd

Please analyze all the samples using the same methodology as your laboratory would use for drinking water samples that are reported under Ontario Regulation 459/00. Please ensure that you complete the methodology questionnaire, as it is critical to helping evaluate the results for this study.

Please report all results and the methodology questionnaire ELECTRONICALLY by **August 16, 2002**.

Please do not hesitate to contact us if you have any questions regarding this interlaboratory study.

Your confidential Study ID Code is: **ID_Code**

Sylvia Cussion
LSB ILS Coordinator
phone:416-235-6348
Fax:416-235-6312
email:cussiosy@ene.gov.on.ca

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N-NITROSODIMETHYLAMINE IN DRINKING WATER
DUE DATE: AUGUST 16, 2002

LABORATORY ID CODE: 220X

1. SAMPLE RECEIPT

Date Samples Received: _____

Date Analysis Initiated: _____

Storage Condition of Samples Prior to Analysis: _____

2. SAMPLE PREPARATION

Sample Volume for Extraction: _____

Extraction Technique: _____

Extraction Solvent: _____

Source of Labeled Standards: _____

When are Labeled Standards introduced to the sample: _____

Final Solvent of Sample: _____

Final Volume of Sample: _____

3. SAMPLE CLEAN-UP

Is a "Clean-up" procedure used: Yes [] No []

Are "Clean-up" Standards added to the sample: Yes [] No []

If "yes", please identify type, source, and when they are added to the sample: _____

Type of "Clean-up" Column: _____

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N-NITROSODIMETHYLAMINE IN DRINKING WATER
DUE DATE: AUGUST 16, 2002

LABORATORY ID CODE: 220X

Other Procedure (eg. adsorbant in a beaker):

Final Solvent of Sample: _____

Final Volume of Sample: _____

4. INSTRUMENTAL ANALYSIS

GC Column: _____

Injection Mode: Splitless _____ On-Column _____ Other: _____

GC Program: _____

Head Pressure: _____ Carrier Gas: _____

Pressure Mode: Constant Pressure _____ Constant Flow _____

Please check the following which applies: GC/LRMS _____ GC/HRMS _____
GC/MS/MS _____ TEA _____ NCLD _____ NPD _____

Manufacturer and Model: _____

Resolution: _____

Source of Calibration Standards: _____

Type of Calibration: single-point [] two-point [] multi-point []

multi-point with continuing calibration []

Addition of further labeled standard to extract immediately prior to instrumental analysis:

Yes [] No []

If "Yes", source and type of standards used: _____

Volume of sample injected: _____

[illegible]

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